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Superconducting energy gap of $BaPb_{1-x}Bi_xO_3$

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We report the first infrared measurement of the superconducting energy gap of $BaPb_{1-x}Bi_xO_3$. In our polycrystalline samples with $T_c \simeq 9.5$ K ($x \simeq 0.2$) we obtain $2\Delta \simeq 3.2kT_c$, roughly in agreement with the weak-coupling Bardeen-Cooper-Schrieffer prediction, $2\Delta = 3.5kT_c$, and with tunneling measurements of the gap. We do not observe any structure above the gap energy associated with strong coupling.

The $BaPb_{1-x}Bi_xO_3$ alloy system of superconductors[1] seems to contradict conventional wisdom, in that it combines a relatively high transition temperature ($T_c \lesssim 12$ K), with a very low electronic density of states at the Fermi level. The mechanism of superconductivity in this system remains unresolved,[2] and has become increasing significant in view of developments in both superconducting Bi oxide[3] and layered Cu oxide compounds.[4] A variety of evidence,[2,5-7] most notably strong phonon structure below 10 meV in tunneling data,[5] points to the conclusion that the high transition temperature of $BaPb_{1-x}Bi_xO_3$ is due to strong coupling to relatively soft phonons.[5-7] This point of view, however, is not easily reconciled with an energy gap, also measured by tunneling,[5] which is not enhanced relative to kT_c as would be expected for conventional strong-coupling superconductivity.[8]

To further explore this problem we have performed far-infrared measurements on $BaPb_{1-x}Bi_xO_3$. Infrared spectroscopy probes much more deeply than tunneling; in $BaPb_{1-x}Bi_xO_3$ the penetration depth is about 5000 Å,[5] whereas the coherence length is less than 100 Å.[5] Like tunneling, infrared can be used to measure both the energy gap and phonon related structure above the gap associated with strong coupling.[9,10] In our experiments we obtain an energy gap consistent with the weak-coupling value, $2\Delta = 3.5T_c$, and we do not observe any strong-coupling structure above 2Δ like that seen in Pb.[9,10] These results suggest that the moderately high T_c of $BaPb_{1-x}Bi_xO_3$ does not arise from strong coupling to soft phonons.

Solid solutions of the type $(1-x)BaPbO_3{:}xBaBiO_3$ were prepared with $x = 0.2$–0.3 $BaCO_3$, PbO, and Bi_2O_3 were mixed and ground together, pressed into pellets, heated to 900 °C/h, and maintained for 10 h. This procedure was repeated three times, with intermediate grindings, using a final firing temperature of 875 °C. The pellets were surrounded by powder of identical composition and contained in covered Pt crucibles during each reaction period. The resulting ceramic samples were found to be single phase by x-ray diffraction, and chemical analysis showed them to be within ± 1% of their expected compositions. A sample with $x \simeq 0.2$ was used for the ir measurement.

In Fig. 1 an ac susceptibility curve shows a transition temperature and width of about 9 K and 1 K, respectively. This measurement is performed on a small piece of the sample used for the infrared measurements shown in Fig. 2. Infrared measurements were made using a Michelson interferometer (10–300 cm^{-1}) to measure reflectivity spectra at roughly 45° incidence as a function of temperature and magnetic field.

To probe the superconducting energy gap we examine ratios of the superconducting to normal-state reflectivity, which are obtained in two ways. In Fig. 2(a) we show the ratio of the reflectivity at $T = 3$ K (superconducting) to that at $T = 10$ K (normal state). The reflectivity in the superconducting state is enhanced relative to that in the normal state at frequencies below about 30 cm^{-1}. This enhancement can be quenched by applying a magnetic field, as shown in Fig. 2(b), where the ratio of the reflectivity at 3 K to a reference reflectivity taken at the same temperature in a large applied magnetic field is shown. In this way we obtain a superconducting to normal-state reflectivity ratio which is essentially equivalent to that in Fig. 2(a). This field-off-field-on ratio contains less spurious noiselike structure because applying a magnetic field disturbs the apparatus less than changing temperature. Experimentally we find that the reflectivity enhancement associated with the superconductivity disappears gradually between 0–3 T, and that above 3 T the change in the reflectivity as a function of magnetic

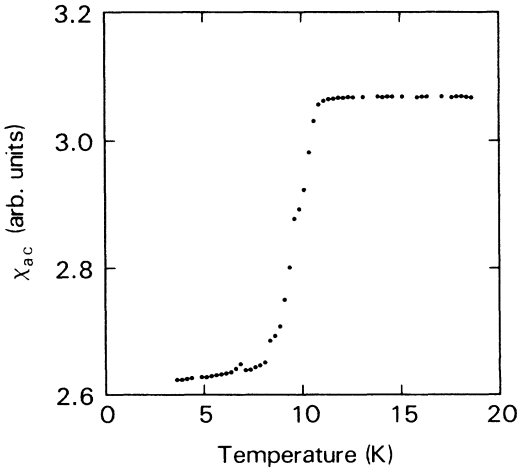

FIG. 1. The ac susceptibility of our composite $BaPb_{1-x}Bi_xO_3$ is shown. A T_c of 9.5 K is estimated.

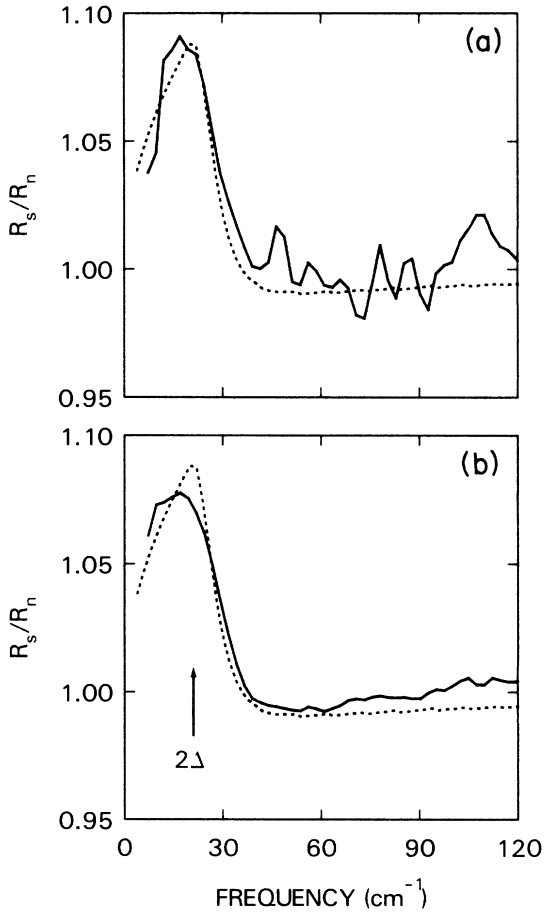

FIG. 2. (a) The measured ratio of the reflectivity in the superconducting state ($T=3$ K) to the reflectivity in the normal state ($T=10$ K) is shown. (b) The measured ratio of the reflectivity at 3 K with and without an applied magnetic field (4 T) is shown (solid line). The dotted curve is a calculated ratio of R_s/R_n with $2\Delta=21$ cm^{-1} as described in the text.

field is negligible. The observation that the infrared reflectivity enhancement associated with the superconductivity is quenched by a field roughly a factor of 3 less than H_{c2} was unexpected, although it appears to be consistent with previous measurements of field dependence of polycrystalline $La_{2-x}Sr_xCuO_4$.[11]

Modeling the reflectivity of $BaPb_{1-x}Bi_xO_3$ is straightforward because its electrodynamic response is nearly isotropic and close to the London (classical) limit. The normal-state reflectivity, R_n, is calculated with a Drude model using a carrier density of 2×10^{21} cm^{-3} and a scattering rate of 8000 cm^{-1} consistent with earlier work on the normal-state reflectivity by Tajima *et al.*[12] In our frequency range R_n closely follows the Hagen-Rubens form, thus the amplitude of the reflectivity ratio, R_s/R_n, at a given frequency below 2Δ is proportional to the square root of the normal-state resistivity. For the superconducting state we use the $T=0$, weak-coupling Mattis-Bardeen form to obtain the conductivity and reflectivity. Below 2Δ the superconducting reflectivity is unity, while at high frequencies $R_s=R_n$. Reasonable agreement between the calculation and the experiment is obtained with $2\Delta=21$ cm^{-1}, as shown in Fig. 2(b). Near 2Δ the measured spectrum is less sharply peaked than the calculated spectrum which may indicate the existence of a distribution of energy gaps in our polycrystalline sample. Gap anisotropy is not expected to play a role since the mean free path is much less that the coherence length. Inasmuch as the the infrared probes vary deeply [~5000 Å (Ref. 5)] in $BaPb_{1-x}Bi_xO_3$, it is unlikely that materials problems associated with the surface, or proximity effects, which can reduce the gap in the region within a coherence length of the surface, will influence the infrared, which is essentially a bulk probe in this dirty, low-carrier-density system. With $T_c=9.5$ K and $2\Delta=21$ cm^{-1} we obtain $2\Delta\simeq3.2kT_c$, consistent, within our experimental accuracy, with the BCS value, $2\Delta=3.5kT_c$.

Tunneling spectra of Batlogg *et al.*[5] show a great deal of phonon structure below ~10 meV, which is the same frequency range in which strong electron-phonon coupling occurs in Pb. If pairing mediated exclusively by such low-frequency modes were responsible for the high T_c of $BaPb_{1-x}Bi_xO_3$, then the coupling strength, and consequently $2\Delta/kT_c$, would have to be even larger than for Pb ($\lambda=1.5$, $T_c=7$ K, $2\Delta/kT_c=4.2$) since T_c is higher. In the conventional pairing theory this enhancement of $2\Delta/kT_c$ is an unavoidable consequence of the thermal pair-breaking effect of the same strongly coupled modes that mediate the pairing.[8] The present infrared measurements, in agreement with previous tunneling measurements of the gap,[5] indicate that $2\Delta/kT_c$ does not have such an enhanced value.

The observation of an energy gap, with roughly the BCS value, and of a substantial isotope shift[13] seems to be consistent with conventional phonon mediated coupling mechanism in $BaPb_{1-x}Bi_xO_3$. Within the conventional framework a coupling spectrum that extends to energies above ~10 meV, with somewhat modest coupling (i.e., $\lambda\lesssim1$) is consistent with the measured gap values and T_c. [Note, however, that even with this restriction the electron-phonon interaction, $V\sim\lambda/N(0)$, may be quite large because $N(0)$ is so small.] The phonon spectrum of $BaPb_{1-x}Bi_xO_3$ has branches which extend to about 35 and 65 meV,[5] either of which is sufficient to produce a T_c of 12 K with a modest coupling, consistent with the measured ratios of 2Δ to kT_c. Reichardt *et al.*[7] have, in fact, noted with surprise that the tunneling spectra show no fidelity with the phonon density of states and have suggested the need to look for evidence of coupling at frequencies above ~10 meV. The higher frequencies modes tend to involve modulation of the (Pb,Bi)—O bond length, including the breathing mode, the possible relevance of which for pairing mediation has been considered.[2] The involvement of still higher frequency, presumably electronic excitations to pairing in $BaPb_{1-x}Bi_xO_3$ is neither supported nor refuted by our observations.

In addition to measuring the superconducting energy gap, we have looked for direct evidence of strong coupling, which can appear in the form of steplike features in R_s/R_n occurring near peaks in $\alpha^2F(\omega-2\Delta)$. These Holstein steps[9,10] have been studied in Pb ($\lambda\simeq1.5$), in which a correspondence between infrared and tunneling data has been established. In $BaPb_{1-x}Bi_xO_3$ we do not observe

any such strong-coupling structure in the infrared response up to about 100 cm^{-1} (12 meV). This is consistent with modest coupling (i.e., $\lambda \lesssim 1$), but does not directly contradict the tunneling observation of phonon structure below 10 meV,[5] since neither technique has provided a normalized measure of the amplitude of $\alpha^2F(\omega)$ for $BaPb_{1-x}Bi_xO_3$.

In conclusion, we have studied the changes in the far-infrared reflectivity of $BaPb_{1-x}Bi_xO_3$ associated with its superconductivity. We find a superconducting energy gap of $2\Delta \simeq 3.2\, kT_c$ and observe no strong-coupling structure above the gap. Predicted on the assumption that the BCS-Eliashberg framework is applicable, these results indicate that the moderately high T_c of $BaPb_{1-x}Bi_xO_3$ does not arise from strong-coupling to soft phonons, but rather from a coupling spectrum that extends to frequencies above ~ 10 meV.

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